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Elaboration of novel polymeric blends with in-situ formation of metallic nanoparticles: water vapour transport properties

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Abstract

Silver nanoparticles exhibit many interesting characteristics like optical properties and catalytic activities. Polymer membranes with in situ formed silver nanoparticles were prepared by dissolving together AgBF4 and poly- (amide 12)-poly(tetramethyleneoxide) block copolymer in an organic medium then evaporating the solvent medium. UV-vis spectroscopic studies evidenced the formation in the solution of silver nanoparticles.

The solid hybrid film changed its color with time under ambient conditions, indicating an evolution of the inorganic matters in the polymer matrix. The transmission electron microscopy showed nanoparticles whose size increases from 18 to 27 nm in the stabilized form in the polymer.

The water vapor uptake in the membranes with different AgBF4 contents studied by microgravimetry allowed us to determine the sorption isotherms at 25°C. The sigmoidal BET-II type isotherms were fairly well fitted with Park's equation, where the concave part was fitted with a Langmuir and a Henry sorption term, while the convex part was fitted with an exponential term in Park's equation that takes into account the clustering of water molecules in the polymer matrix. We suggest that at low water activity, water molecules adsorb on Langmuir sites-probably on the nanoparticle surface-and at high activities water molecules form aggregates in the polymer matrix.

PACS: Type pacs here, separated by semicolons ;

Keywords: PA12-PTMO copolymer membranes ; Silver nanoparticles; Park's equation; Water molecules clustering.

1. Introduction

Olefin/paraffin separation using facilitated transport membranes is of great interest in petrochemical industries [1-14]. Recently, several studies on solid polymer membranes containing silver salt as carriers for the facilitated transport of olefin have been reported [4-14]. Polymers such as poly (2-ethyl-2-oxazoline) (POZ), poly (vinylpyrrolidone) (PVP), cellulose acetate, polyether-block-amide (PEBA) [15] containing polar groups in their

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chains have been used as polymer matrix to dissolve the silver salts for the olefin-facilitated transport. Despite the extremely high separation performance of silver polymer electrolyte membranes, an important question remains about their applications; the long-term stability of their separation performance is in doubt because silver ions can be reduced to form silver metal nanoparticles and thus lose their olefin carrier activity [16-18].

Kang and coworkers [19] succeeded in preparing dispersed silver nanoparticles in several polymer systems (POZ, PVP, polyphenylene oxide, poly (ethylene phthalate). The catalytic activities of those systems were not studied, but the catalytic activities of silver nanoparticles embedded in poly (N-isopropylacrylamide) shells of poly (styrene) particles were reported for the reaction of nitrophenol reduction [26]. Silver nanoparticles exhibit rich optical properties which can be tuned by controlling the particle size and geometry [27].Therefore, the stabilization of the silver ions, confined in the membrane matrix, is a challenging topic as it could lead to promising impacts on membrane science and separation technology. In this study we will examine the effect of light irradiation of PEBA/ $AgBF_4$ samples on their stability. PebaxTM polymers are interesting block-copolymer materials, since they are industrially produced and used for different goods. Nanocomposites using those polymers would benefit from the high mechanical performances of PebaxTM materials and the specific properties of the nanoparticles. In the present work, we study first the effect of UV irradiation of PebaxTM/AgBF4 solutions on the formed nanoparticles. Next the water vapor sorption characteristics of the membranes with nanoparticles are studied by microgravimetry, and the data are analyzed on the basis of sorption models. The water sorption data are always useful, since materials are often in contact with water vapor in their applications in air.

2. Experimental

2.1. *Materials*

The PA12-co-PTMO granulates (Pebax 2533) were kindly provided by Ato-Fina Corp. Its density as measured with a Micromeritics Accupyc 1330 instrument was 1.01 g/cm^3, and its Shore D hardness was 25. This Pebax grade contains 25 wt. % of PA12 blocks, and 75 wt.% of PTMO blocks. All other chemicals were purchased from Aldrich and used without further purification. The membranes were prepared by dissolving first the copolymer in ethanol at 75°C to obtain a 2 wt. % solution. In the same time, an appropriate mass of $AgBF_4$ was dissolved in DMF (dimethylformamid), then the obtained solution was dissolved in Pebax solution, and the obtained dopes were cast onto a glass plate with a Gardner knife and the membranes were slowly dried in ambient air first, then under vacuum. The membrane thickness was ca. 100µm. The membrane samples were used shortly after their preparation, as the membrane darkens in long storage.

2.2. *Characterization*

The IR measurements were performed on an AVATAR 360 Nicolet series FT-IR spectrometer; 32 scans were signal averaged at a resolution of 4 cm^{-1} [19,20]. Transmission electron micrographs (TEM) were obtained using a Tecrai 12 microscope operating at 120 Kv, in order to monitor the sizes and quantities of silver metal nanoparticles in the membranes resulting from the reduction of silver ions [21]. Specimens for TEM were prepared by casting a DMF solution of Pebax 2533 (2%) containing $AgBF_4$ on a glass plate and drying for 2h under 60°C. After the specimens had completely dried, they were placed onto a standard TEM copper grid. UV-vis spectra were measured with a Scinco UV S-2100 spectrophotometer using quartz cells.

3. Results and discussion

Upon mixing $AgBF_4$ in ethanol with Pebax in a weight ratio of $AgBF_4$/Pebax = 0.5/100, a clear yellow solution was obtained, and the intensity of the yellow coloration increased rapidly with time. The deep yellow color of the solution was maintained at least for 1 week and then became light red. Figure 1 shows the UV-vis spectra of the solution containing $AgBF_4$ and Pebax recorded at time intervals. As indicated by the yellowich coloration, a characteristic silver band appears at 420 nm. The mechanism for the formation of silver nanoparticles will be discussed later. The effect of the weight ratio of $AgBF_4$/Pebax on the silver nanoparticle formation was investigated

using UV-vis spectroscopy. Figure 2 shows the UV-vis spectra of the solutions with the weight ratios of $AgBF_4$/Pebax of 0.5, 1.5, and 2.5 wt% $AgBF_4$. The silver band shifts to a high wavelength with increasing weight ratio of $AgBF_4$/Pebax. As explained by Heard et al [22] and Henglein [23], the band shift to a higher wavelength can be attributed to the difference in the size and distribution of the particles. To confirm the correlation between silver band shift and particle size, TEM micrographs were taken on the membranes samples prepared from the precedent solutions. Figure 3 shows the TEM and the corresponding size histograms of silver metal nanoparticles for the Pebax/$AgBF_4$ membranes with 0.5 and 1.5 wt% $AgBF_4$ membranes immediately after preparation. Silver metal nanoparticles are possibly formed during the sample preparation procedure and are present in both samples, but the number and size of silver nanoparticles in 1.5 wt% $AgBF_4$ Pebax/$AgBF_4$ sample are much larger than for 0.5 wt% $AgBF_4$ one. Figure 4 shows the TEM micrographs taken after 1 month storage in a vacuum oven. The TEM image clearly shows that the number and size of silver metal nanoparticles in 0.5 wt % $AgBF_4$ Pebax/$AgBF_4$ sample are much smaller than in the 1.5 wt % $AgBF_4$ one. The total number of particles in the membrane containing 1.5 wt % $AgBF_4$ does not change significantly, but their average particle diameter was found to have increased markedly, from 19.86 to 27.25 nm. The formation of silver metal nanoparticles in the membranes is indicated by the change in color of the membranes from colorless to dark brown. The interaction between silver ions and the carbonyl oxygens of PEBAX was investigated using FT-IR spectroscopy. Figure 5 shows that the spectrum of pure Pebax® has a characteristic peak at 1730 cm^{-1} which is attributed to the –C=O stretching vibration. Another peaks at 1646 indicates the presence of H–N–C=O groups. When $AgBF_4$ salt is incorporated the peak at 1646 cm^{-1} shifts to 1635 cm^{-1}. The shift to a lower wavenumber is due to the loosening of the C=O bond interaction that arises from the electron donation by the C=O oxygens to the silver ions. Thus, the degree of the C=O peak shift indicates the intensity of the interaction between the C=O groups and the silver ions.

3.1. Sorption characteristics

The water vapor sorption isotherm in a Pebax 2533/$AgBF_4$ membranes is representated in Fig. 6. Its shaps is actually sigmoïdal and similar to the BET II or type 5 system. The concavity of the isotherm with respect to the activity axis at low activities as far as upturn is attributed to dual-mode sorption, which is made up of Henry's and Langmuir's components. The first one (Henry type) is the illustration of random water absorption (dissolution) in the polymer matrix. The second one (Langmuir) occurs when special adsorption sites are present in the polymer. In the water-Pebax/$AgBF_4$ system, microvoids or unrelaxed volumes existing in every glassy structure. The glassy structure of the matrix has its origin in the high rigidity brought by the polyamide chains.

Park [24] has described the water clustering process by the following equilibrium:

$$n(H_2O) \Leftrightarrow (H_2O)_n \qquad \text{(Eq.1)}$$

a multi-mode isotherm Eq. (2) was deduced

$$C = \frac{Ab_L a}{1 + b_L a} + \frac{K_C s^n a^n}{n} + sa \qquad \text{(Eq. 2)}$$

where C is the concentration of water, a the activity of water, K_C the equilibrium constant for the clustering reaction (1), s the Henry's type solubility coefficient, n the mean number of water molecules per cluster, A the Langmuir capacity constant and b_L the Langmuir affinity constant. In Eq. (2), the first term represents the Langmuir sorption, the second the clustering and the third Henry's law. According to the sorption mode existing at low water activities, the first term is effectively present or not. Park used this equation to examine the sigmoïdal sorption of the water-polyacrylonitrile system studied by Stannet et al. [25]. Therefore the isotherm in Fig. 3 has been described analytically by Park's equation (Eq. 1), the five parameters of which (A, b_L, K_C, s, n) were estimated by the following methodology. After calculating the water concentration in the polymer (C expressed in $cm^3STP_{sorbed\ water}\ g^{-1}_{dry\ polymer}$) from experimental water uptake, a linear regression was applied to the first points (before upturn) of the isotherms to determine s, A and b_L, so as to estimate the concentration of water (C_{DM}) attributed to dual-mode over the complete activity range ($0<a<1$), then, the concentration of water assumed to be due to the clustering (C_{ag}) was calculated by substraction of C_{DM} from C_{ag} by applying a linear regression to the last points after upturn with eqn. (3):

$$\ln C_{ag} = f(\ln(k_a a)) \qquad \text{Eqn. (3)}$$

whose n value is obtained from the slope, and $\ln K_C/n$ from the intercept.

3.2. Dependence of the sorption characteristics of membranes on silver amount

The sorption isotherms of water vapor obtained with Pebax-$AgBF_4$ membranes loaded with varying weight percentage of $AgBF_4$ are showed in figure 7. Those isotherms are analyzed with use of Park's model. The different values of Park's parameters are resumed in Table 1. we can see that all the isotherms have a similar evolution since the membranes have almost the same thickness (sample 1%: 78µm; sample 2%: 80µm; sample 10%: 83µm).

3.3. Park's Parameters

The figure 7 shows the capacity of Park's equation to describe sigmoïdal isotherms. The curves reconstructed from the last equation smooth the experimental points with satisfaction. However, a little variation is observed in the case of high activities. The K_c and n values increase with increasing of weight percent of $AgBF_4$ in membranes (Fig 8). Those two parameters are influenced by the last point (a= 0.85) of the isotherm. The b_L is relative to the initial slope of isotherm. Its value is slightly incertain because of miss of data in the beginning of curve. A broad range of error is attributed to this last parameter and its variation is enough little significative.

4. Conclusion

The silver nanoparticles formation was investigated by the change of coloration of PA12-PTMO/$AgBF_4$ solution which changes from incolor to yellowich. The adding of salt to the prepared solutions generates a variation of size and distribution of silver particles in the membrane. The exposition of membranes to light during 10 days takes inchangeable the number and distribution of nanoparticles, but genrate the increasing of mean diameter of particles.

The sigmoïdal shape of the water vapor isotherms in Pebax 2533-AgBF4 is of BET II type. This obtained isotherm is decomposed in three sorption modes: Henry's, Langmuir's and clustering. These three types of sorption are resumed in Park's phenomenological equation versus activity. Good agreement is obtained between experimental and calculated values from Park's law, except for a slight deviation at high activities owing to aggregation phenomenon.

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